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(54) **Coated cemented carbide endmill having hard-materials-coated-layers excellent in adhesion**

Sinterkarbideschaftfräser beschichtet mit Hartstoffschichten mit hervorragenden  
Adhäsionseigenschaften

Fraise à queue en carbure fritté pourvue de couches en matériaux durs ayant une excellente adhésion

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**Description****BACKGROUND OF THE INVENTION**5    **1. Field of the Invention**

**[0001]** The present invention relates to a coated cemented carbide endmill exhibiting excellent wear resistance for a long period of time because even if the endmill is used in high speed cutting, the hard-material-coated-layers of the endmill are not exfoliated due to the excellent adhesion thereof.

10    **2. Description of the Related Art**

**[0002]** Conventionally, there is known coated cemented carbide endmills composed of a tungsten carbide (hereinafter, shown by WC) based cemented carbide substrate (hereinafter, simply referred to as a cemented carbide substrate) having a surface portion to which formed, in an average layer thickness of 0.5 - 5 µm, are hard-material-coated-layers composed of a Ti compound layer which is composed of one or more layers of a Titanium carbide (TiC), Titanium nitride (TiN), Titanium carbide-nitride (TiCN), Titanium oxy-carbide (TiCO), Titanium oxy-nitride (TiNO) and Titanium oxy-carbo-nitride (TiCNO), each of the hard-material-coated-layers being formed by medium temperature chemical vapor deposition (a method generally referred to as MT-CVD by which vapor deposition is performed at 700 - 980°C which is relatively lower than the vapor deposition temperature 1000 - 1150°C employed by ordinary high temperature chemical vapor deposition (hereinafter, referred to as HT-CVD)), as shown in, for example, Japanese Unexamined Patent Publication No. 62-88509.

**[0003]** Recently, since labor and energy are greatly saved in a cutting process, there is a tendency that a cutting speed as one of cutting conditions is further more increased accordingly. When the conventional coated cemented carbide endmills are used under such high speed condition, the hard-material-coated layers are liable to be exfoliated due to their insufficient adhesion, by which the endmills are remarkably worn and their life is ended in a relatively short time.

**[0004]** To cope with this problem, the inventors directed attention to the conventional coated cemented carbide endmills from the above point of view and made studies to improve the adhesion of the hard-material-coated layers constituting the endmills. As a result, the inventors have obtained a conclusion that when a coated cemented carbide endmill is arranged as shown in the following items (a), (b) and (c), the adhesion of the Ti compound layer to the surface of the cemented carbide substrate of the endmill is greatly improved by a surface layer which is formed to the surface portion thereof by being heated at a high temperature and thus the hard-material-coated layer of the coated cemented carbide endmill is not exfoliated even if the endmill is used in high speed cutting and the endmill exhibits excellent wear resistance for a long time:

(a) the cemented carbide substrate has a composition of 5 - 20 wt% of Co (hereinafter, % shows wt%) as a binder phase forming component, further when necessary, 0.1 - 2% of one kind or two kinds of Cr and V as the binder phase forming component, further when necessary, 0.1 - 5% of one kind or more kinds of carbides, nitrides and carbonitrides of Ti, Ta, Nb and Zr (hereinafter, shown as TiC, TiN, TiCN, TaC, TaN, TaCN, NbC, NbN, NbCN, ZrC, ZrN and ZrCN, respectively) as well as two or more kinds of solid solutions thereof (hereinafter, they are shown as (Ti, Ta, Nb, Zr) C·N as a whole) as a dispersed phase forming component and the balance being WC as the dispersed phase forming component and inevitable impurities, wherein the WC has a refined particle structure having an average particle size of 0.1 - 1.5 µm;

(b) when the cemented carbide substrate shown in (a) is heated at a high temperature in a hydrogen atmosphere in which a carbon dioxide gas or titanium tetrachloride is blended under conditions that the atmosphere is set to a pressure of 50 - 550 torr and the substrate is held at a temperature of 900 - 1000°C for 1 - 15 minutes, a surface layer created by the reaction of composite carbides of Co and W (hereinafter, shown by  $Co_mW_nC$ ) is formed to the surface portion of the base substance over a predetermined depth from the uppermost surface at the cutting edge thereof.

(c) hard-material-coated layers composed of a Ti compound layer and, when necessary, an aluminum oxide (hereinafter, shown by  $Al_2O_3$ ) layer are formed to the surface of the substrate having the surface layer which is formed by being heated at the high temperature and in which the reaction-created  $Co_mW_nC$  shown in (b) is distributed, wherein the Ti compound layer is composed of one or more layers of a TiC, TiN, TiCN, TiCO, TiNO and TiCNO using MT-CVD and the aluminum oxide layer is formed using MT-CVD or HT-CVD.

## SUMMARY OF THE INVENTION

[0005] The present invention achieved based on the result of the above studies is characterized in a coated cemented carbide endmill having hard-material-coated layers excellent in an adhesion, the endmill comprising a tungsten carbide

5 based cemented carbide substrate having a composition of 5 - 20 wt% of Co as a binder phase forming component, further when necessary, 0.1 - 2% of one kind or two kinds of Cr and V as the binder phase forming component, further when necessary, 0.1 - 5% of one kind or more kinds of (Ti, Ta, Nb, Zr) C·N as a dispersed phase forming component and the balance being WC as the dispersed phase forming component and inevitable impurities, wherein the WC has a refined particle structure having an average particle size of 0.1 - 1.5 µm, the cemented carbide substrate has a  
10 surface layer formed to the surface portion thereof which is formed by being heated at a high temperature and in which reaction-created  $Co_mW_nC$  is distributed over a depth of 0.1 - 2 µm from the uppermost surface at the cutting edge thereof and further the substrate has coated layers composed of a Ti compound layer and, further when necessary, an  $Al_2O_3$  layer formed thereto in an average layer thickness of 0.5 - 4.5 µm, the Ti compound layer being composed of one or more layers of a TiC, TiN, TiCN, TiCO, TiNO and TiCNO using MT-CVD and the  $Al_2O_3$  layer being formed  
15 using MT-CVD or HT-CVD.

[0006] Next, reasons why the compositions of the cemented carbide substrate constituting the coated cemented carbide endmill of the present invention, the average particle size of WC particles and the distributed depth of  $Co_mW_nC$  and the average layer thickness of the hard-material-coated layers are limited as described above will be described.

20 (a) Co content

[0007] Co has an action for improving a sinterability and thereby improving the toughness of the cemented carbide substrate. When a Co content is less than 5%, however, a desired toughness improving effect cannot be obtained, whereas when the Co content is larger than 20%, not only the wear resistance of the cemented carbide substrate itself  
25 is lowered but also the cemented carbide substrate is deformed by the heat generated in high speed cutting. Thus, the Co content is set to 5 - 20% and preferably to 8 - 12%.

(b) Cr and V

30 [0008] Cr and V are contained in a necessary amount because they are dissolved in solid in Co as the binder phase forming component to thereby strengthen it as well as contribute to refine the WC particles and further have an action for promoting the formation of the reaction-created  $Co_mW_nC$  which is distributed in the surface layer formed by being heated at the high temperature to thereby improve the adhesion of the hard-material-coated layers achieved by the reaction-created  $Co_mW_nC$ . When their content is less than 0.1%, however, it cannot be expected that the above action  
35 achieves a desired effect, whereas when their content is larger than 2%, the above action is saturated and an improving effect cannot be further enhanced. Thus, their content is set to 0.1 - 2% and preferably to 4 - 0.8%.

[0009] When the coated cemented carbide endmill is made, it is preferable that Cr and V as the binder phase forming component are used in the form of carbides, nitrides and oxides of Cr and V (hereinafter, shown as  $Cr_3C_2$ ,  $CrN$ ,  $Cr_2O_3$ ,  
40  $VC$ ,  $VN$  and  $V_2O_5$  and further shown as (Cr, V) C·N·O as a whole) as material powders. Since these material powders are dissolved in solid in Co as the binder phase forming component when sintering is carried out and form a binder phase, a precipitate containing Cr and V as one of components cannot be observed by an optical microscope or a scanning electron microscope.

(c) (Ti, Ta, Nb, Zr) C·N

45 [0010] Since these components have an action for improving the wear resistance of the cemented carbide substrate, they are contained in a necessary amount. When their content is less than 0.1%, however, a desired wear resistance improving effect cannot be obtained, whereas when it is larger than 5%, toughness is lowered. Thus, their content is set to 0.1 - 5% and preferably 1 - 2.5%.

50 (d) Average particle size of WC

[0011] It is intended to improve the strength of the cemented carbide substrate by the refined particle structure of WC particles and the refined particle structure is obtained by setting the particle size of WC powder used as material powder to 1.5 µm or less. Accordingly, when the average particle size of the material powder is larger than 1.5 µm, a  
55 desired strength improving effect cannot be obtained, whereas when it is less than 0.1 µm, wear resistance is lowered. Thus, the average particle size of the WC powder is set to 0.1 - 1.5 µm and preferably to 0.6 - 1.0 µm.

(e) Average distributed depth of  $\text{Co}_m\text{W}_n\text{C}$ 

[0012] Since the portion of the endmill which contributes to cutting is a cutting edge and the portion of the endmill which is far from the cutting edge does not contribute to the cutting, the average distributed depth of  $\text{Co}_m\text{W}_n\text{C}$  is important at the portion of the cutting edge. Thus, the average distributed depth will be prescribed here. When the average distributed depth of  $\text{Co}_m\text{W}_n\text{C}$  is less than 0.1  $\mu\text{m}$ , the ratio of it distributed in the surface layer formed by being heated at the high temperature is too small for the  $\text{Co}_m\text{W}_n\text{C}$  to secure a desired excellent adhesion to the hard-material-coated layers, whereas when the average distributed depth thereof is larger than 2  $\mu\text{m}$ , since ratio of the average distributed depth of the  $\text{Co}_m\text{W}_n\text{C}$  in the uppermost surface portion of the cemented carbide substrate is made excessively large, chipping is liable to be caused to a cutting edge. Thus, the average distributed depth is set to 0.1 - 2  $\mu\text{m}$  and preferably to 0.5 - 1.5  $\mu\text{m}$ .

## (f) Average layer thickness of the hard-material-coated layers

[0013] When the average layer thickness of the hard-material-coated layers is less than 0.5  $\mu\text{m}$ , desired excellent wear resistance cannot be obtained, whereas when the average layer thickness is larger than 4.5  $\mu\text{m}$ , chipping is liable to be caused to the cutting edge.

Thus, the average layer thickness is set to 0.5 - 4.5  $\mu\text{m}$  and preferably to 1.5 - 2.5  $\mu\text{m}$ .

## 20 DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0014] A coated cemented carbide endmill of the present invention will be specifically described with reference to embodiments.

## 25 (Embodiment 1)

[0015] WC powder having a predetermined average particle size within the range of 0.1 - 1.5  $\mu\text{m}$ , various carbide powder, nitride powder and carbo-nitride powder each having the average particle size of 0.5  $\mu\text{m}$  as shown in Table 1 and Table 2 and constituting (Ti, Ta, Nb, Zr) C·N and Co powder having the average particle size of 0.5  $\mu\text{m}$  were prepared as material powders. These material powders were blended to the composition shown in Table 1 and Table 2 likewise, wet mixed in a ball mill for 72 hours and dried and thereafter pressed to green compact at the pressure of 1 ton/cm<sup>2</sup> and the green compact was vacuum sintered under conditions that it was held for one hour in the vacuum of  $1 \times 10^{-3}$  torr at a predetermined temperature within the range of 1350 - 1500°C and cemented carbide substrates a - z which had compositions substantially similar to the above blended compositions and comprised WC particles having the average particle sizes shown in Table 1 and Table 2 were formed.

[0016] Further, cemented carbide substrates A - Z were made by forming a surface layer formed by being heated at a high temperature to the surface portion of each of the cemented carbide substrates a - z under the conditions shown in Table 3 and Table 4, the surface having  $\text{Co}_m\text{W}_n\text{C}$  distributed therein over the average depths shown in Table 3 and Table 4.

[0017] Subsequently, hard-material-coated layers having the compositions and the average layer thicknesses shown in Table 6 and Table 7 were formed under the conditions shown in Table 5 to the surface of each of the cemented carbide substrates A - Z and coated cemented carbide ball-nose endmills of the present invention (hereinafter, referred to as coated endmills of the present invention) 1 - 26 were made. The endmills were composed of a shank portion and a two-flute portion and had a ball-nose radius of 5 mm and a helix angle of 30°.

[0018] For the purpose of comparison, comparative coated cemented carbide endmills (hereinafter, referred to as comparative coated endmill) 1 - 26 were made, respectively under conditions similar to the above conditions except that cemented carbide substrates a - z, to which the surface layer formed by being heated at the high temperature was not formed, were used in place of the cemented carbide substrates A - Z having the above surface layer as shown in Table. 8.

[0019] Next, high speed copy milling was carried out, by means of the resultant coated endmills 1 - 26 of the present invention and the resultant comparative coated endmills 1 - 26, to alloy steel in a dry state by alternately effecting down-cut and up-cut milling under the following conditions and the width of the maximum flank face of the cutting edge of each of the endmills was measured.

55 material to be cut SKD61 (hardness: HR( : 53)  
cutting speed: 800 m/min  
feed per tooth: 0.1 mm/cutting edge  
depth of cut: 0.5 mm

width of cut: 0.5 mm  
length of cut: 250 m

Since the comparative coated endmills 1 - 26 were worn at a high speed, the cutting operation of them was interrupted 5 when the width of the maximum flank wear of the cutting edge reached 0.3 mm and the cut length up to that time was measured. Table 6 - Table 8 show the result of measurement, respectively.

## (Embodiment 2)

10 [0020] WC powder having a predetermined average particle size within the range of 0.1 - 1.5 µm, Cr<sub>3</sub>C<sub>2</sub> powder having the average particle size of 0.5 µm, VC powder having the average particle size of 0.5 µm and Co powder having the average particle size of 0.5 µm were prepared as material powders. These material powders were blended at a predetermined blend ratio, wet mixed in a ball mill for 72 hours and dried and thereafter pressed to green compact at the pressure of 1 ton/cm<sup>2</sup> and the green compact was vacuum sintered under conditions that it was held for one 15 hour in the vacuum of  $1 \times 10^{-3}$  torr at a predetermined temperature within the range of 1350 - 1500°C and cemented carbide substrates a - t which had the compositions shown in Table 9 and comprised WC having the average particle sizes shown in Table 9 were formed.

[0021] Further, cemented carbide substrates A - T were made by forming a surface layer formed by being heated at a high temperature to the surface portion of each of the cemented carbide substrates a - z under the conditions shown 20 in Table 10, the surface layer having Co<sub>m</sub>W<sub>n</sub>C distributed therein over the average depths shown in Table 10.

[0022] Subsequently, hard-material-coated layers having the compositions and the average layer thicknesses shown 25 in Table 12 were formed under the conditions shown in Table 11 to the surface of each of the cemented carbide substrates A - T and coated cemented carbide ball-nose endmills of the present invention (hereinafter, referred to as coated endmills of the present invention) 1 - 20 were made, respectively. The endmills were composed of a shank portion and a two-flute portion and had a ball-nose radius of 5 mm and a helix angle of 30°.

[0023] For the purpose of comparison, comparative coated cemented carbide endmills (hereinafter, referred to as 30 comparative coated endmills) 1 - 20 were made, respectively under conditions similar to the above conditions except that cemented carbide substrates a - t, to which the surface layer formed by being heated at the high temperature was not formed, were used in place of the cemented carbide substrates A - T having the above surface layer as shown in Table. 13.

[0024] Next, high speed copy milling was carried out, by means of the resultant coated endmills 1 - 20 of the present invention and the resultant comparative coated endmills 1 - 20, to alloy steel in a dry state by alternately effecting down-cut and up-cut milling under the following conditions and the worn width of the maximum flank face of the cutting edge of each of the endmills was measured.

35 material to be cut: SKD61 (hardness: HR : 53)  
cutting speed: 500 m/min  
feed per tooth: 0.1 mm/cutting edge  
depth of cut: 0.5 mm  
40 width of cut: 0.5 mm  
length of cut: 350 m

Table 12 and Table 13 show the result of measurement, respectively.

## (Embodiment 3)

[0025] WC powder having a predetermined average particle size within the range of 0.1 - 1.5 µm, various carbide powder, nitride powder, oxide powder and carbo-nitride powder each having the average particle size of 0.5 µm and constituting (Ti, Ta, Nb, Zr) C-N and (Cr, V) C-N-O, Co powder having the average particle size of 0.5 µm and carbon 50 powder for adjusting an amount of carbon were prepared as material powders. These material powders were blended to a predetermined composition, wet mixed in a ball mill for 72 hours and dried and thereafter pressed to green compact at the pressure of 1 ton/cm<sup>2</sup> and the green compact was vacuum sintered under conditions that it was held for one hour in the vacuum of  $1 \times 10^{-3}$  torr at a predetermined temperature in the range of 1350 - 1500°C and cemented carbide substrates a - s which had the compositions shown in Table. 14 and comprised WC particles having the average 55 particle sizes shown in Table 14 were formed.

[0026] Further, cemented carbide substrates A - S were made by forming a surface layer formed by being heated at a high temperature to the surface portion of each of the cemented carbide substrates a - s under the conditions shown in Table 15, the surface layer having Co<sub>m</sub>W<sub>n</sub>C distributed therein over the average depths shown in Table 15.

[0027] Subsequently, hard-material-coated layers having the compositions and the average layer thicknesses shown in Table 17 were formed under the conditions shown in Table 16 to the surface of each of the cemented carbide substrates A - S and coated carbide ball-nose endmills of the present invention (hereinafter, referred to as coated endmills of the present invention) 1 - 19 were made. The endmills were composed of a shank portion and a two-flute portion and had a ball-nose radius of 5 mm and a helix angle of 30°.

[0028] For the purpose of comparison, comparative coated cemented carbide endmills (hereinafter, referred to as comparative coated endmills) 1 - 19 were made, respectively under conditions similar to the above conditions except that cemented carbide substrates A - S, to which the surface layer formed by being heated at the high temperature was not formed, were used in place of the cemented carbide substrates A - S having the above surface layer as shown in Table.

[0029] Next, high speed copy milling was carried out, by means of the resultant coated endmills 1 - 19 of the present invention and the resultant comparative coated endmills 1 - 19, to alloy steel in a dry state by alternately effecting down-cut and up-cut milling, under the following conditions and the width of the maximum flank wear of the cutting edge of each of the endmills was measured.

material to be cut: SKD61 (hardness: HR<sub>C</sub> : 53)  
 cutting speed: 650 m/min  
 feed per tooth: 0.1 mm/cutting edge  
 depth of cut: 0.5 mm  
 width of cut: 0.5 mm  
 time of cut: 50 min

Table 17 and Table 18 show the result of measurement, respectively.

[0030] It is apparent from the results shown in Tables 6 - 8, 12, 13, 17 and 18 that the hard-material-coated layers of the coated endmills of the present invention were not exfoliated and the endmills thereby exhibited excellent wear resistance, whereas the hard-material-coated layers of the comparative coated endmills were exfoliated in the midway of cutting and the endmills were greatly worn by the exfoliation and their life was ended in a relatively short time.

[0031] In the coated carbide endmills of the present invention, since the adhesion of the hard-material-coated layers to the surface of the cemented carbide substrate is greatly improved by the ComWnC distributed in the surface layer formed to the surface portion of the base substance by being heated at the high temperature as described above, the hard-material-coated layers are not exfoliated not only when the endmills are used under usual cutting conditions but also even if they are used in high speed cutting. Accordingly, the coated cemented carbide endmills of the present invention exhibit excellent wear resistance for a long period of time.

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Table 1

Type	Composition (wt%)	Average grain size of WC ( $\mu\text{m}$ )
Cemented carbide substrate	a Co: 5, WC + impurities: balance	1.2
	b Co: 8, WC + impurities: balance	0.8
	c Co: 10, WC + impurities: balance	1.0
	d Co: 12, WC + impurities: balance	1.2
	e Co: 15, WC + impurities: balance	0.6
	f Co: 20, WC + impurities: balance	0.4
	g Co: 13, TiN: 2.5, WC + impurities: balance	0.4
	h Co: 10, TaC: 2, WC + impurities: balance	0.8
	i Co: 6, NbC: 0.5, WC + impurities: balance	1.2
	j Co: 5, ZrCN: 0.1, WC + impurities: balance	1.5
	k Co: 7, (Ti, Ta) N: 0.8, WC + impurities: balance	1.0
	l Co: 15, (Ti, Nb) CN: 3.5, NbCN: 0.5, WC + impurities: balance	0.5
30	m Co: 8, (Ti, Zr) CN: 1, WC + impurities: balance	0.6
	n Co: 8, (Ta, Nb) C: 1.5, WC + impurities: balance	1.0

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Table 2

Type	Composition (wt%)	Average grain size of WC ( $\mu\text{m}$ )
Cemented carbide substrate	o Co: 12, (Ta, Zr) C: 2, WC + impurities: balance	0.6
	p Co: 6, (Zr, Nb) N: 1.2, NbN: 0.3, WC + impurities: balance	1.2
	q Co: 10, (Ti, Ta, Nb) C: 2.2, WC + impurities: balance	0.8
	r Co: 20, (Ti, Ta, Zr) N: 5, WC + impurities: balance	0.1
	s Co: 12, (Ti, Zr, Nb) CN: 2.5, WC + impurities: balance	0.6
	t Co: 8, (Ta, Nb, Zr) C: 1, TiCN: 0.5, WC + impurities: balance	1.2
	u Co: 6, (Ti, Ta, Zr, Nb) C: 1, WC + impurities: balance	0.8
	v Co: 10, TaN: 1.5, TiC: 0.5, WC + impurities: balance	1.2
	w Co: 7, (Ti, Zr) C: 0.4, ZrN: 0.1, WC + impurities: balance	0.8
	x Co: 17, (Ti, Zr) N: 1, (Ti, Ta, Zr) C: 3, TaCN: 0.6, WC + impurities: balance	1.5
30	y Co: 12, TiC: 0.2, ZrC: 0.8, (Ta, Nb) C: 1, WC + impurities: balance	1.0
	z Co: 15, TiN: 0.5, TaC: 1, ZrCN: 1, NbC: 0.5, WC + impurities: balance	0.4

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Table 3

5	Type	Symbol of substrate	Surface layer formed by being heated at high temperature				
			Forming conditions			Average distributed depth of $\text{Co}_m\text{W}_n\text{C}$ ( $\mu\text{m}$ )	
10			Atmosphere		Temperature (°C)	Holding time (min.)	
15			Ratio of composition blended to $\text{H}_2$ (volt)	Pressure (torr)			
20	Cemented carbide substrate	A	$\text{CO}_2$ : 11	250	950	6	1.64
		B	$\text{TiCl}_4$ : 2	550	900	11	0.83
		C	$\text{CO}_2$ : 10	300	950	10	1.27
		D	$\text{TiCl}_4$ : 3	400	920	7	0.80
		B	$\text{CO}_2$ : 10	50	900	5	0.24
		F	$\text{TiCl}_4$ : 2	150	900	5	0.41
		G	$\text{TiCl}_4$ : 2	450	900	10	1.73
		H	$\text{CO}_2$ : 11	350	950	12	1.48
		I	$\text{CO}_2$ : 9	550	1000	15	2.00
		J	$\text{TiCl}_4$ : 1	300	950	10	0.99
		K	$\text{TiCl}_4$ : 3	50	1000	5	0.45
		L	$\text{CO}_2$ : 11	200	950	5	1.28
		M	$\text{CO}_2$ : 9	80	900	6	0.31

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Table 4

5	Type	Symbol of substrate	Surface layer formed by being heated at high temperature					
			Forming conditions			Average distributed depth of $\text{Co}_m\text{W}_n\text{C}$ ( $\mu\text{m}$ )		
10			Atmosphere		Temperature (°C)	Holding time (min.)		
15			Ratio of composition blended to $\text{H}_2$ (volt)	Pressure (torr)				
20	Cemented carbide substrate	N	n	$\text{TiCl}_4$ : 1	250	900	13	1.02
25		O	o	$\text{TiCl}_4$ : 3	450	950	11	0.56
30		P	p	$\text{CO}_2$ : 9	300	1000	13	1.52
35		Q	q	$\text{CO}_2$ : 10	500	950	15	1.80
40		R	r	$\text{TiCl}_4$ : 1	100	900	6	0.53
45		S	s	$\text{TiCl}_4$ : 3	450	1000	14	1.45
50		T	t	$\text{CO}_2$ : 11	500	1000	15	1.82
55		U	u	$\text{TiCl}_4$ : 1	50	900	5	0.11
60		V	v	$\text{TiCl}_4$ : 3	100	900	7	0.36
65		W	w	$\text{CO}_2$ : 9	300	950	9	1.01
70		X	x	$\text{TiCl}_4$ : 2	450	900	10	1.98
75		Y	y	$\text{CO}_2$ : 11	100	900	6	0.33
80		Z	z	$\text{TiCl}_4$ : 2	400	950	8	1.81

Table 5

40	Type of hard-material-coated-layer	Hard-material-coated-layer forming conditions		
		Composition of reaction gas (vol%)	Reaction atmosphere	
45	$\text{Al}_2\text{O}_3$ *	$\text{Al}_2\text{Cl}_3$ : 4, $\text{CO}_2$ : 10, $\text{H}_2\text{S}$ : 0.2, $\text{HCl}$ : 2, $\text{H}_2$ : balance	50	1020
50	$\text{Al}_2\text{O}_3$	$\text{Al}[\text{OCH}(\text{CH}_3)_2]_3$ : 0.3, $\text{H}_2$ : balance	50	900
55	TiC	$\text{TiCl}_4$ : 2, $\text{C}_3\text{H}_8$ : 5, $\text{H}_2$ : balance	100	900
60	TiN	$\text{TiCl}_4$ : 2, N : 30, H : balance	100	850
65	TiCN	$\text{TiCl}_4$ : 2, $\text{N}_2$ : 10, $\text{CH}_3\text{CN}$ : 0.8, H: balance	70	900
70	TiCO	$\text{TiCl}_4$ : 3, CO: 2, $\text{H}_2$ : balance	100	900

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Table 5 (continued)

5	Type of hard-material-coated-layer	Hard-material-coated-layer forming conditions	
		Composition of reaction gas (vol%)	Reaction atmosphere
10	TiNO	TiCl <sub>4</sub> : 3, CO: 1, N <sub>2</sub> : 15, H <sub>2</sub> : balance	Pressure (torr) 50 Temperature (°C) 900
	TiCNO	TiCl <sub>4</sub> : 3, CO: 2, N <sub>2</sub> : 15, H <sub>2</sub> : balance	50 900
[In Table 5, item with * shows high temperature chemical vapor deposition (HT-CVD) and items without * show medium temperature chemical vapor deposition (MT-CVD).]			

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Table 6

Type	Symbol of substrate	Hard-material-coated-layer (average layer thickness is shown in parentheses, unit: µm)					Width of max-blank wear of cutting edge
		First layer	Second layer	Third layer	Fourth layer	Fifth layer	
Coated carbide endmill of the present invention	A	TiCN(0.9)	TiCNO(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.5)*	TiCNO(0.1)	TiN(0.3)	0.13
	B	TiC(0.5)	TiCNO(0.3)	Al <sub>2</sub> O <sub>3</sub> (0.2)	--	--	0.09
	C	TiN(0.1)	TiCN(1.8)	TiCNO(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.3)*	TiN(0.2)	0.06
	D	TiC(1.9)	TiCNO(0.5)	TiN(0.1)	--	--	0.10
	E	TiN(0.8)	TiCN(0.2)	--	--	--	0.19
	F	TiCN(2.0)	--	--	--	--	0.18
	G	TiCN(0.3)	TiCNO(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.1)	--	--	0.15
	H	TiCN(1.6)	Al <sub>2</sub> O <sub>3</sub> (0.4)*	--	--	--	0.05
	I	TiN(0.1)	TiC(0.5)	TiCN(0.9)	--	--	0.18
	J	TiC(1.0)	TiCN(0.9)	TiCND(0.1)	Al <sub>2</sub> O <sub>3</sub> (1.0)	--	0.13
	K	TiC(0.1)	TiCN(4.4)	--	--	--	0.18
	L	TiN(0.5)	TiC(2.5)	Al <sub>2</sub> O <sub>3</sub> (0.5)*	--	--	0.12
	M	TiCN(1.3)	TiN(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.4)*	TiN(0.2)	--	0.10

[In Table 6, item with \* shows hard-material-coated-layer made by high temperature chemical vapor deposition and items without \* show hard-material-coated-layers made by medium temperature chemical vapor deposition, respectively.]

Table 7

Type	Symbol of substrate	Hard-material-coated-layer (average layer thickness is shown in parentheses, unit/in)					Width of maximum wear of cutting edge
		First layer	Second layer	Third layer	Fourth layer	Fifth layer	
Coated carbide endmill of the present invention	14 N	TiCN(0.1)	TiCN(1.2)	TiCN(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.2)*	--	0.07
	15 O	TiC(0.5)	TiCN(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.1)	--	--	0.09
	16 P	TiN(0.1)	TiC(2.0)	TiCN(2.0)	TiCN(0.1)	TiCN(0.3)	0.17
	17 Q	TiN(0.1)	TiCN(1.4)	TiN(0.1)	--	--	0.17
	18 R	TiN(0.1)	TiCN(1.0)	TiC(1.0)	TiCN(0.5)	Al <sub>2</sub> O <sub>3</sub> (0.2)*	0.13
	19 S	TiN(0.2)	TiCN(1.0)	TiCN(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.2)	--	0.09
	20 T	TiN(0.5)	TiC(1.0)	TiCN(1.5)	TiN(0.5)	--	0.19
	21 U	TiN(0.1)	TiCN(1.0)	TiCN(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.1)	--	0.14
	22 V	TiCN(4.0)	TiN(0.5)	--	--	--	0.18
	23 W	TiN(0.1)	TiCN(2.1)	Al <sub>2</sub> O <sub>3</sub> (0.3)*	--	--	0.09
	24 X	TiN(0.5)	--	--	--	--	0.20
	25 Y	TiCN(0.3)	TiCN(1.4)	Al <sub>2</sub> O <sub>3</sub> (0.1)*	--	--	0.10
	26 Z	TiCN(3.0)	Al <sub>2</sub> O <sub>3</sub> (0.5)	--	--	--	0.12

[In Table 7, items with \* show hard-material-coated-layers made by high temperature chemical vapor deposition and items without \* show hard-material-coated-layers made by medium temperature chemical vapor deposition, respectively.]

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Table 8

Type	Symbol of substrate	Hard-material-coated-layer	Result of cutting test	Type	Symbol of substrate	Hard-material-coated-layer	Result of cutting test
Comparative coated carbide endmill	a	similar to coated carbide endmill 1 of the present invention	life ended in 175 m	Comparative coated carbide endmill	14	n	similar to coated carbide endmill 14 of the present invention
	b	similar to coated carbide endmill 2 of the present invention	life ended in 150 m		15	o	similar to coated carbide endmill 15 of the present invention
	c	similar to coated carbide endmill 3 of the present invention	life ended in 200 m		16	p	similar to coated carbide endmill 16 of the present invention
	d	similar to coated carbide endmill 4 of the present invention	life ended in 125 m		17	q	similar to coated carbide endmill 17 of the present invention
	e	similar to coated carbide endmill 5 of the present invention	life ended in 125 m		18	r	similar to coated carbide endmill 18 of the present invention
	f	similar to coated carbide endmill 6 of the present invention	life ended in 150 m		19	s	similar to coated carbide endmill 19 of the present invention
	g	similar to coated carbide endmill 7 of the present invention	life ended in 150 m		20	t	similar to coated carbide endmill 20 of the present invention
	h	similar to coated carbide endmill 8 of the present invention	life ended in 200 m		21	u	similar to coated carbide endmill 21 of the present invention
	i	similar to coated carbide endmill 9 of the present invention	life ended in 125 m		22	v	similar to coated carbide endmill 22 of the present invention
	j	similar to coated carbide endmill 10 of the present invention	life ended in 150 m		23	w	similar to coated carbide endmill 23 of the present invention
	k	similar to coated carbide endmill 11 of the present invention	life ended in 100 m		24	x	similar to coated carbide endmill 24 of the present invention
	l	similar to coated carbide endmill 12 of the present invention	life ended in 150 m		25	y	similar to coated carbide endmill 25 of the present invention
	m	similar to coated carbide endmill 13 of the present invention	life ended in 200 m		26	z	similar to coated carbide endmill 26 of the present invention

Table 9

Type	Composition (wt%)				Average grain size of WC ( $\mu\text{m}$ )	
	Co	Cr	V	WC + impurities		
Cemented carbide substrate	a	8.1	0.52	0.10	balance	0.52
	b	9.8	0.40	0.21	balance	0.76
	c	7.8	0.28	0.12	balance	0.95
	d	10.3	0.11	0.30	balance	0.83
	e	12.4	0.23	0.45	balance	0.51
	f	11.6	0.78	0.22	balance	0.80
	g	19.7	1.71	0.31	balance	0.11
	h	15.1	0.13	0.08	balance	1.23
	i	18.2	-	1.52	balance	0.30
	j	7.9	-	0.61	balance	1.17
	k	5.0	-	0.11	balance	1.50
	l	9.6	-	0.48	balance	0.82
	m	6.3	-	0.29	balance	0.12
	n	19.8	-	0.13	balance	1.54
	o	10.1	0.82	-	balance	1.04
	p	8.0	0.55	-	balance	0.51
	q	6.1	0.32	-	balance	1.47
	r	17.8	1.54	-	balance	0.33
	s	15.2	0.96	-	balance	0.80
	t	12.0	1.03	-	balance	0.49

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Table 10

Type	Symbol of substrate	Surface layer formed by being heated at high temperature				
		Forming conditions			Average distributed depth of $\text{Co}_m\text{W}_n\text{C}$ ( $\mu\text{m}$ )	
		Atmosphere		Temperature (°C)	Holding time (min.)	
		Ratio of composition blended to $\text{H}_2$ (vol%)	Pressure (torr)			
Comected carbide substrate	A	$\text{CO}_2$ : 11	230	1000	3	0.96
	B	$\text{TiCl}_4$ : 2	450	950	1	0.52
	C	$\text{CO}_2$ : 9	350	1000	10	1.52
	D	$\text{TiCl}_4$ : 2	550	900	7	1.04
	E	$\text{TiCl}_4$ : 3	500	1000	7	1.30
	F	$\text{TiCl}_4$ : 1	300	900	7	0.48
	G	$\text{TiCl}_4$ : 2	50	900	1	0.12
	H	$\text{CO}_2$ : 9	200	950	3	0.31
	I	$\text{TiCl}_4$ : 1	400	950	7	1.06
	J	$\text{TiCl}_4$ : 2	450	950	7	1.33
	K	$\text{CO}_2$ : 10	550	1000	10	1.95
	L	$\text{CO}_2$ : 9	250	950	5	0.51
	M	$\text{TiCl}_4$ : 3	850	1000	7	1.80
	N	$\text{CO}_2$ : 9	500	1000	10	1.76
	O	$\text{TiCl}_4$ : 2	400	950	5	0.97
	P	$\text{TiCl}_4$ : 2	500	950	10	1.45
	Q	$\text{TiCl}_4$ : 3	200	900	3	0.30
	R	$\text{TiCl}_4$ : 1	350	950	10	1.89
	S	$\text{CO}_2$ : 10	100	900	1	0.26
	T	$\text{CO}_2$ : 11	200	950	3	0.47

Table 11

Type of hard-material-coated-layer	Hard-material-coated-layer forming conditions		
	Composition of reaction gas (vol%)	Reaction atmosphere	
$\text{Al}_2\text{O}_3^*$	$\text{Al}_2\text{Cl}_3$ : 4, $\text{CO}_2$ : 10, $\text{H}_2\text{S}$ : 0.2, $\text{HCl}$ : 2, $\text{H}_2$ : balance	Pressure (torr)	Temperature (°C)

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Table 11 (continued)

5	Type of hard-material-coated-layer	Hard-material-coated-layer forming conditions	
		Composition of reaction gas (vol%)	Reaction atmosphere
10	Al <sub>2</sub> O <sub>3</sub>	Al[OCH(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> : 0.3, H <sub>2</sub> : balance	50 900
15	TiC	TiCl <sub>4</sub> : 2, C <sub>3</sub> H <sub>8</sub> : 5, H <sub>2</sub> : balance	100 900
20	TiN	TiCl <sub>4</sub> : 2, N <sub>2</sub> : 30, H <sub>2</sub> : balance	100 850
25	TiCN	TiCl <sub>4</sub> : 2, N <sub>2</sub> : 10, CH <sub>3</sub> CN: 0.8, H <sub>2</sub> : balance	70 900
30	TiCO	TiCl <sub>4</sub> : 3, CO: 2, H <sub>2</sub> : balance	100 900
35	TiNO	TiCl <sub>4</sub> : 3, CO: 1, N <sub>2</sub> : 15, H <sub>2</sub> : balance	50 900
40	TiCNO	TiCl <sub>4</sub> : 3, CO: 2, N <sub>2</sub> : 15, H <sub>2</sub> : balance	50 900

[In Table 11, item with \* shows high temperature chemical vapor deposition (HT-CVD) and items without \* show medium temperature chemical vapor deposition (MT-CVD).]

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Table 12

Type	Symbol of substrate	Hard-material-coated-layer (average layer thickness is shown in parentheses, $\mu$					Worn width of max-clank wear of cutting edge
		First layer	Second layer	Third layer	Fourth layer	Fifth layer	
coated carbide and/or of the present invention	1 A	TiN(0.2)	TiCN(3.0)	TiCN(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.2)	--	0.05
	2 B	TiCN(0.3)	TiCN(1.4)	Al <sub>2</sub> O <sub>3</sub> (0.1)*	--	--	0.06
	3 C	TiCN(2.0)	--	--	--	--	0.18
	4 D	TiCN(1.6)	Al <sub>2</sub> O <sub>3</sub> (0.4)*	--	--	--	0.07
	5 E	TiN(0.1)	TiCN(2.0)	TiCN(2.0)	TiN(0.1)	TiN(0.3)	0.19
	6 F	TiN(1.0)	TiCN(2.8)	Al <sub>2</sub> O <sub>3</sub> (0.5)*	--	--	0.09
	7 G	TiN(0.5)	TiCN(1.0)	TiCN(1.5)	TiN(0.5)	--	0.18
	8 H	TiCN(0.9)	TiCN(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.3)*	TiCN(0.1)	TiN(0.1)	0.11
	9 I	TiCN(0.5)	TiCN(0.3)	Al <sub>2</sub> O <sub>3</sub> (0.2)	--	--	0.12
	10 J	TiN(0.8)	TiCN(0.2)	--	--	--	0.08
	11 K	TiCN(1.3)	TiN(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.4)*	TiN(0.2)	--	0.09
	12 L	TiN(0.1)	TiCN(0.6)	TiCN(0.9)	--	--	0.15
	13 M	TiCN(0.3)	TiCN(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.1)	--	--	0.12
	14 N	TiN(0.6)	--	--	--	--	0.19
	15 O	TiN(0.1)	TiCN(1.2)	TiCN(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.1)	--	0.08
	16 P	TiN(0.1)	TiCN(2.1)	Al <sub>2</sub> O <sub>3</sub> (0.3)*	--	--	0.07
	17 Q	TiCN(1.0)	TiCN(0.9)	TiCN(0.1)	Al <sub>2</sub> O <sub>3</sub> (1.0)	--	0.11
	18 R	TiCN(1.9)	TiCN(0.5)	TiN(0.1)	--	--	0.15
	19 S	TiN(0.1)	TiCN(1.4)	TiN(1.0)	--	--	0.16
	20 T	TiCN(0.1)	TiCN(4.4)	--	--	--	0.19

[In Table 12, items with \* show hard-material-coated-layers made by high temperature chemical vapor deposition and items without \* show hard-material-coated-layers made by medium temperature chemical vapor deposition, respectively.]

Table 13

Type	Symbol of substrate	Hard-material-coated-layer					Width of max-flank wear of cutting edge
		First layer	Second layer	Third layer	Fourth layer	Fifth layer	
Comparative coated carbide endmill	1 a	similar to coated carbide endmill 1 of the present invention					0.32
	2 b	similar to coated carbide endmill 2 of the present invention					0.34
	3 c	similar to coated carbide endmill 3 of the present invention					0.43
	4 d	similar to coated carbide endmill 4 of the present invention					0.31
	5 e	similar to coated carbide endmill 5 of the present invention					0.42
	6 f	similar to coated carbide endmill 6 of the present invention					0.35
	7 g	similar to coated carbide endmill 7 of the present invention					0.41
	8 h	similar to coated carbide endmill 8 of the present invention					0.35
	9 i	similar to coated carbide endmill 9 of the present invention					0.38
	10 j	similar to coated carbide endmill 10 of the present invention					0.31
	11 k	similar to coated carbide endmill 11 of the present invention					0.33
	12 l	similar to coated carbide endmill 12 of the present invention					0.40
	13 m	similar to coated carbide endmill 13 of the present invention					0.37
	14 n	similar to coated carbide endmill 14 of the present invention					0.46
	15 o	similar to coated carbide endmill 15 of the present invention					0.32
	16 p	similar to coated carbide endmill 16 of the present invention					0.32
	17 q	similar to coated carbide endmill 17 of the present invention					0.37
	18 r	similar to coated carbide endmill 18 of the present invention					0.39
	19 s	similar to coated carbide endmill 19 of the present invention					0.43
	20 t	similar to coated carbide endmill 20 of the present invention					0.44

Table 14

Type	Composition (wt%)						Average grain size of WC ( $\mu\text{m}$ )
	Co	Cr	V	(Ti, Ta, Nb, Zr)	C + N	WC + impurities	
Cemented carbide substrate							
a	12.0	0.48	0.50	TiC: 1.9		balance	0.9
b	7.9	0.23	1.02	TaN: 0.5		balance	1.2
c	14.6	1.41	-	TaCN: 1.5		balance	0.4
d	10.1	1.42	0.51	NbN: 1.3		balance	0.5
e	17.8	-	1.55	NbCN: 3.3		balance	0.2
f	5.3	-	0.10	ZrCN: 0.9		balance	1.3
g	9.8	0.52	-	TaC: 1.0		balance	1.0
h	12.1	-	0.16	NbC: 3.0		balance	0.5
i	7.8	0.39	-	ZrN: 1.2		balance	1.5
j	14.7	-	1.21	TiCN: 4.1		balance	1.0
k	5.0	0.20	-	TiN: 0.5		balance	1.0
l	15.2	1.23	-	ZrC: 2.3		balance	0.3
m	11.9	1.04	-	(Ta, Nb) C: 1.5		balance	0.5
n	10.2	0.79	-	TaC: 0.5, ZrN: 0.5		balance	0.8
o	5.3	-	0.17	(Ti, Ta, Zr) C: 0.1		balance	1.5
p	19.8	0.87	0.97	(Ti, Ta, Nb, Zr) C: 5.0		balance	0.1
q	8.1	-	0.39	(Ti, Zr) C: 1.0, NbC: 0.1		balance	1.2
r	16.9	-	1.98	(Ta, Nb) C: 0.5, TaC: 1.0		balance	0.5
s	9.8	0.89	-	TiC: 0.2, TaN: 0.8 NbC: 0.2, ZrCN: 1.6		balance	0.5

Table 15

Type	Symbol of substrate	Surface layer formed by being heated at high temperature				
		Forming conditions			Average distributed depth of $\text{Co}_m\text{W}_n\text{C}$ ( $\mu\text{m}$ )	
		Atmosphere		Temperature ( $^{\circ}\text{C}$ )	Holding time (min.)	
		Ratio of composition blended to $\text{H}_2$ (vol%)	Pressure (torr)			
Cemented carbide substrate	A	$\text{CO}_2$ : 9	500	950	13	1.22
	B	$\text{TiCl}_4$ : 3	350	950	8	0.54
	C	$\text{CO}_2$ : 11	400	900	15	1.01
	D	$\text{TiCl}_4$ : 2	250	950	6	0.87
	E	$\text{CO}_2$ : 10	150	950	2	0.30
	F	$\text{TiCl}_4$ : 1	400	1000	8	1.13
	G	$\text{CO}_2$ : 11	350	900	5	0.42
	H	$\text{TiCl}_4$ : 2	350	950	10	1.04
	I	$\text{CO}_2$ : 10	400	1000	15	1.53
	J	$\text{TiCl}_4$ : 3	450	900	13	1.31
	K	$\text{TiCl}_4$ : 3	550	1000	15	1.94
	L	$\text{CO}_2$ : 9	500	950	10	0.87
	M	$\text{TiCl}_4$ : 2	350	950	6	0.45
	N	$\text{CO}_2$ : 10	400	920	8	0.51
	O	$\text{CO}_2$ : 11	200	900	4	0.34
	P	$\text{CO}_2$ : 9	50	900	2	0.11
	Q	$\text{TiCl}_4$ : 1	300	1000	3	0.80
	R	$\text{TiCl}_4$ : 1	150	950	7	0.23
	S	$\text{TiCl}_4$ : 2	100	900	5	0.17

Table 16

Type of hard-material-coated-layer	Hard-material-coated-layer forming conditions		
	Composition of reaction gas (vol%)	Reaction atmosphere	
		Pressure (torr)	Temperature ( $^{\circ}\text{C}$ )
$\text{Al}_2\text{O}_3$ *	$\text{Al}_2\text{Cl}_3$ : 4, $\text{CO}_2$ : 10, $\text{H}_2\text{S}$ : 0.2, $\text{HCl}$ : 2, $\text{H}_2$ : balance	50	1020

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Table 16 (continued)

5	Type of hard-material-coated-layer	Hard-material-coated-layer forming conditions		
		Composition of reaction gas (vol%)	Reaction atmosphere	
10			Pressure (torr)	Temperature (°C)
Al <sub>2</sub> O <sub>3</sub>	Al[OCH(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> : 0.3, H <sub>2</sub> : balance		50	900
TiC	TiCl <sub>4</sub> : 2, C <sub>3</sub> H <sub>8</sub> : 5, H <sub>2</sub> : balance		100	900
TiN	TiCl <sub>4</sub> : 2, N <sub>2</sub> : 30, H <sub>2</sub> : balance		100	850
TiCN	TiCl <sub>4</sub> : 2, N <sub>2</sub> : 10, CH <sub>3</sub> CN: 0.8, H <sub>2</sub> : balance		70	900
TiCO	TiCl <sub>4</sub> : 3, CO: 2, H <sub>2</sub> : balance		100	900
TiNO	TiCl <sub>4</sub> : 3, CO: 1, N <sub>2</sub> : 15, H <sub>2</sub> : balance		50	900
TiCNO	TiCl <sub>4</sub> : 3, CO: 2, N <sub>2</sub> : 15, H <sub>2</sub> : balance		50	900

[In Table 16, item with \* shows high temperature chemical vapor deposition (HT-CVD) and items without \* show medium temperature chemical vapor deposition (MT-CVD).]

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Table 17

Type	Symbol of substrate	Hard-material-coated-layer (average layer thickness is shown in parentheses, $\mu$ in)				Width of flank wear of cutting edge
		First layer	Second layer	Third layer	Fourth layer	
coated carbide and all of the present invention	1 A	TiN(0.1)	TiCN(0.5)	TiC(0.5)	Al <sub>2</sub> O <sub>3</sub> (0.1)*	TiN(0.1)
	2 B	TiCN(2.1)	Al <sub>2</sub> O <sub>3</sub> (0.3)*	TiN(0.2)	--	--
	3 C	TiC(3.5)	TiCO(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.3)	--	--
	4 D	TiN(0.2)	TiCN(2.0)	TiC(0.3)	Al <sub>2</sub> O <sub>3</sub> (0.2)	--
	5 E	TiN(2.0)	--	--	--	--
	6 F	TiCN(0.9)	Al <sub>2</sub> O <sub>3</sub> (0.1)	--	--	--
	7 G	TiN(0.1)	TiCN(3.0)	TiCO(0.9)	TiCO(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.4)*
	8 H	TiC(3.0)	--	--	--	--
	9 I	TiN(0.1)	TiCN(1.8)	TiN(0.1)	--	--
	10 J	TiC(2.0)	TiN(1.0)	--	--	--
	11 K	TiCN(0.5)	--	--	--	--
	12 L	TiC(2.0)	Al <sub>2</sub> O <sub>3</sub> (0.5)	--	--	--
	13 M	TiN(0.2)	TiCN(2.0)	TiNO(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.5)*	TiN(0.2)
	14 N	TiN(0.1)	TiCN(1.0)	TiCO(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.5)*	--
	15 O	TiCN(1.5)	Al <sub>2</sub> O <sub>3</sub> (0.5)	--	--	--
	16 P	TiCN(2.9)	TiCO(0.2)	Al <sub>2</sub> O <sub>3</sub> (0.4)	--	--
	17 Q	TiC(1.7)	TiCO(0.1)	Al <sub>2</sub> O <sub>3</sub> (0.2)	--	--
	18 R	TiCN(1.5)	TiN(0.1)	TiCN(1.5)	TiC(0.5)	Al <sub>2</sub> O <sub>3</sub> (0.4)*
	19 S	TiN(0.1)	TiCN(0.5)	TiCO(0.5)	Al <sub>2</sub> O <sub>3</sub> (0.2)	--

[In Table 17, item with \* shows hard-material-coated-layer made by high temperature chemical vapor deposition and items without \* show hard-material-coated-layers made by medium temperature chemical vapor deposition, respectively.]

Table 18

Type	Symbol of substrate	Hard-material-coated-layer	Result of cutting test
Comparative coated carbide endmill	1	a similar to coated carbide endmill 1 of the present invention	life ended in 40 min
	2	b similar to coated carbide endmill 2 of the present invention	life ended in 40 min
	3	c similar to coated carbide endmill 3 of the present invention	life ended in 35 min
	4	d similar to coated carbide endmill 4 of the present invention	life ended in 45 min
	5	e similar to coated carbide endmill 5 of the present invention	life ended in 20 min
	6	f similar to coated carbide endmill 6 of the present invention	life ended in 45 min
	7	g similar to coated carbide endmill 7 of the present invention	life ended in 45 min
	8	h similar to coated carbide endmill 8 of the present invention	life ended in 20 min
	9	i similar to coated carbide endmill 9 of the present invention	life ended in 20 min
	10	j similar to coated carbide endmill 10 of the present invention	life ended in 25 min
	11	k similar to coated carbide endmill 11 of the present invention	life ended in 20 min
	12	l similar to coated carbide endmill 12 of the present invention	life ended in 30 min
	13	m similar to coated carbide endmill 13 of the present invention	life ended in 45 min
	14	n similar to coated carbide endmill 14 of the present invention	life ended in 45 min
	15	o similar to coated carbide endmill 15 of the present invention	life ended in 40 min
	16	p similar to coated carbide endmill 16 of the present invention	life ended in 30 min
	17	q similar to coated carbide endmill 17 of the present invention	life ended in 35 min
	18	r similar to coated carbide endmill 18 of the present invention	life ended in 45 min
	19	s similar to coated carbide endmill 19 of the present invention	life ended in 40 min
(life is ended by exfoliation of hard-material-coated-layer in any case)			

## Claims

- 55 1. A coated cemented carbide endmill having hard-material-coated layers excellent in an adhesion, comprising a tungsten carbide based cemented carbide substrate, wherein the tungsten carbide has a refined particle structure having average particle size of 0.1 - 1.5  $\mu\text{m}$ , the tungsten carbide substrate has a surface layer in which carbide ( $\text{Co}_m\text{W}_n\text{C}$ ) are distributed over a depth of 0.1 - 2  $\mu\text{m}$  from the uppermost surface at the cutting edge thereof and

further the cemented carbide substrate has the hard-material-coated layers composed of Ti compound layer formed thereto in an average layer thickness of 0.5 - 4.5 µm, the Ti compound layer being composed of one or more layers of TiC, TiN, TiCN, TiCO, TiNO, TiCNO.

- 5        2. A coated cemented carbide endmill having hard-material-coated layers excellent in an adhesion, comprising a tungsten carbide based cemented carbide substrate, wherein the tungsten carbide has a refined particle structure having average particle size of 0.1 - 1.5 µm, the tungsten carbide substrate has a surface layer in which carbide ( $Co_mW_nC$ ) are distributed over a depth of 0.1- 2 µm from the uppermost surface at the cutting edge thereof and further the cemented carbide substrate has the hard-material-coated layers composed of Ti compound layer and  $Al_2O_3$  layer formed thereto in an average layer thickness of 0.5 - 4.5 µm, the Ti compound layer being composed of one or more layers of TiC, TiN, TiCN, TiCO, TiNO, TiCNO.
- 10      3. A coated cemented carbide endmill having hard-material-coated layers excellent in an adhesion, comprising a tungsten carbide based cemented carbide substrate, wherein the tungsten carbide has a refined particle structure having average particle size of 0.1 - 1.5 µm, the tungsten carbide substrate has a surface layer formed to the surface portion thereof which is formed by being heated at a high temperature and in which carbide ( $Co_mW_nC$ ) created by the reaction of Co and W are distributed over a depth of 0.1- 2 µm from the uppermost surface at the cutting edge thereof and further the cemented carbide substrate has the hard-material-coated layers composed of Ti compound layer formed thereto in an average layer thickness of 0.5 - 4.5 µm, the Ti compound layer being composed of one or more layers of TiC, TiN, TiCN, TiCO, TiNO, TiCNO formed by medium temperature chemical vapor deposition at a temperature of 700 - 980 °C.
- 15      4. A coated cemented carbide endmill having hard-material-coated layers excellent in an adhesion, comprising a tungsten carbide based cemented carbide substrate, wherein the tungsten carbide has a refined particle structure having average particle size of 0.1 - 1.5 µm, the tungsten carbide substrate has a surface layer formed to the surface portion thereof which is formed by being heated at a high temperature and in which carbide ( $Co_mW_nC$ ) created by the reaction of Co and W are distributed over a depth of 0.1- 2 µm from the uppermost surface at the cutting edge thereof and further the cemented carbide substrate has the hard-material-coated layers composed of Ti compound layer and  $Al_2O_3$  layer formed thereto in an average layer thickness of 0.5 - 4.5 µm, the Ti compound layer being composed of one or more layers of TiC, TiN, TiCN, TiCO, TiNO, TiCNO formed by medium temperature chemical vapor deposition at a temperature of 700 - 980 °C.
- 20      5. A coated cemented carbide endmill according to Claim 1 to 4, wherein said cemented carbide substrate have a composition of 5 - 20 wt% of Co as a binder phase forming component and the balance being tungsten carbide as a dispersed phase forming component and inevitable impurities.
- 25      6. A coated cemented carbide endmill according to Claim 1 to 4, wherein said cemented carbide substrate have a composition of 5 - 20 wt% of Co as a binder phase forming component, 0.1 - 2 wt% of Cr and/or V as a binder phase forming component and the balance being tungsten carbide as a dispersed phase forming component and inevitable impurities,
- 30      7. A coated cemented carbide endmill according to Claim 1 to 4, wherein said cemented carbide substrate have a composition of 5 - 20 wt% of Co as a binder phase forming component, 0.1 - 5 wt% of one or more kinds of carbides and nitrides of Ti, Ta, Nb and Zr as well as two or more kinds of solid solutions thereof as a dispersed phase forming component and the balance being tungsten carbide as a dispersed phase forming component and inevitable impurities.
- 35      8. A coated cemented carbide endmill according to Claim 1 to 4, wherein said cemented carbide substrate have a composition of 5 - 20 wt% of Co as a binder phase forming component, 0.1 - 2 wt% of Cr and/or V as a binder phase forming component, 0.1 - 5 wt% of one or more kinds of carbides and nitrides of Ti, Ta, Nb and Zr as well as two or more kinds of solid solutions thereof as a dispersed phase forming component and the balance being tungsten carbide as a dispersed phase forming component and inevitable impurities.

#### 55      Patentansprüche

1. Beschichteter Sinterhartmetall-Schaftfräser, welcher Schichten aus Hartstoffen mit hervorragender Adhäsion aufweist, umfassend ein Sinterhartmetallsubstrat auf Wolframcarbid-Basis, wobei das Wolframcarbid eine verfeinerte

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Partikelstruktur mit einer mittleren Partikelgröße von 0,1 - 1,5 µm aufweist, das Wolframcarbid-Substrat eine Oberflächenschicht aufweist, in der Carbid ( $\text{Co}_m\text{W}_n\text{C}$ ) über eine Tiefe von 0,1 - 2 µm von der äußersten Oberfläche der Schneidkante an verteilt ist, und wobei das Sinterhartmetall-Substrat darüber hinaus Hartstoffschichten aufweist, die aus einer Ti-Verbindungs-Schicht aufgebaut sind, welche darauf in einer mittleren Schichtdicke von 0,5 - 4,5 µm ausgebildet sind, wobei die Ti-Verbindungs-Schicht aus einer oder mehr Schichten aus TiC, TiN, TiCN, TiCO, TiNO, TiCNO aufgebaut ist.

2. Beschichteter Sinterhartmetaif-Schaftfräser, welcher Schichten aus Hartstoff mit hervorragender Adhäsion aufweist, umfassend ein Sinterhartmetall-Substrat auf Wolframcarbid-Basis, wobei das Wolframcarbid eine verfeinerte Partikelstruktur mit einer mittleren Partikelgröße von 0,1 - 1,5 µm aufweist, das Wolframcarbid-Substrat eine Oberflächenschicht aufweist, in der Carbid ( $\text{Co}_m\text{W}_n\text{C}$ ) über eine Tiefe von 0,1 - 2 µm von der äußersten Oberfläche der Schneidkante an verteilt ist, und wobei das Sinterhartmetall-Substrat darüber hinaus Hartstoffschichten aufweist, welche aus einer Ti-Verbindungs-Schicht und einer  $\text{Al}_2\text{O}_3$ -Schicht aufgebaut sind, welche darauf in einer mittleren Schichtdicke von 0,5 - 4,5 µm ausgebildet sind, wobei die Ti-Verbindungs-Schicht aus einer oder mehr Schichten aus TiC, TiN, TiCN, TiCO, TiNO, TiCNO aufgebaut ist.
3. Beschichteter Sinterhartmetall-Schaftfräser, welcher Schichten aus Hartstoff mit hervorragender Adhäsion aufweist, umfassend ein Sinterhartmetall-Substrat auf Wolframcarbid-Basis, wobei das Wolframcarbid eine verfeinerte Partikelstruktur mit einer mittleren Partikelgröße von 0,1 - 1,5 µm aufweist, wobei das Wolframcarbid-Substrat eine Oberflächenschicht aufweist, die im Oberflächenbereich ausgebildet ist und geformt wird durch Erwärmen auf eine hohe Temperatur, und in der Carbid ( $\text{Co}_m\text{W}_n\text{C}$ ), welches durch Reaktion von Co und W gebildet wird, über eine Tiefe von 0,1 - 2 µm von der äußersten Oberfläche der Schneidkante an verteilt ist und wobei das Sinterhartmetall-Substrat Hartstoffschichten aufweist, die aus einer Ti-Verbindungs-Schicht aufgebaut sind, welcher in einer Schichtdicke von 0,5 - 4,5 µm ausgebildet ist, wobei die Ti-Verbindungs-Schicht aus einer oder mehr Schichten aus TiC, TiN, TiCN, TiCO, TiNO, TiCNO aufgebaut ist und durch chemische Mitteltemperatur-Dampfabscheidung bei einer Temperatur von 700 - 980 °C gebildet wird.
4. Beschichteter Sinterhartmetall-Schaftfräser, welcher Hartstoffschichten mit hervorragender Adhäsion aufweist, umfassend ein Sinterhartmetall-Carbid-Substrat auf Wolframcarbid-Basis, wobei das Wolframcarbid eine verfeinerte Partikelstruktur mit einer mittleren Partikelgröße von 0,1 - 1,5 µm aufweist, das Wolframcarbid-Substrat eine Oberflächenschicht im Oberflächenbereich aufweist, welche durch Erwärmen auf eine hohe Temperatur gebildet wird und in der durch Reaktion von Co und W gebildetes Carbid ( $\text{Co}_m\text{W}_n\text{C}$ ) über eine Tiefe von 0,1 µm von der äußersten Oberfläche der Schneidkante an teilt ist und darüber hinaus das Sinterhartmetall-Substrat Hartstoffschichten aufweist, die aus einer Ti-Verbindungs-Schicht und einer  $\text{Al}_2\text{O}_3$ -Schicht aufgebaut sind, die darauf in mittlerer Schichtdicke von 0,5 - 4,5 µm ausgebildet sind, wobei die Ti-Verbindungs-Schicht aus einer oder mehr Schichten von TiC, TiN, TiCN, TiCO, TiNO, TiCNO aufgebaut ist, die durch chemische Mitteltemperatur-Dampfabscheidung bei einer Temperatur von 700 - 980 °C gebildet werden.
5. Beschichteter Sinterhartmetall-Schaftfräser nach Anspruch 1 - 4, wobei das Sinterhartmetall-Substrat eine Zusammensetzung von 5 - 20 Gew.-% Co als Binderphase, die eine Komponente bildet, aufweist, und der Rest Wolframcarbid als eine dispergierte Phase bildende Komponente und unvermeidbare Verunreinigungen ist.
6. Beschichteter Sinterhartmetall-Schaftfräser nach Anspruch 1 - 4, wobei das Sinterhartmetall-Substrat eine Zusammensetzung von 5 - 20 Gew.-% Co als Binderphase bildende Komponente, 0,1 - 2 Gew.-% Cr und/oder V als Binderphase bildende Komponente aufweist, und der Rest Wolfram-Carbid als dispergierte Phase bildende Komponente und unvermeidbare Verunreinigungen ist.
7. Beschichteter Sinterhartmetall-Schaftfräser nach Anspruch 1 - 4, wobei das Sinterhartmetall-Substrat eine Zusammensetzung aus 5 - 20 Gew.-% Co als Binderphase bildende Komponente, 0,1 - 5 Gew.-% von einer oder mehr Arten von Carbiden und Nitriden von Ti, Ta, Nb und Zr genauso wie zwei oder mehr Arten fester Lösungen davon als dispergierte Phase bildende Komponente aufweist, und der Rest Wolframcarbid als dispergierte Phase bildende Komponente und unvermeidbare Verunreinigungen ist.
8. Beschichteter Sinterhartmetall-Schaftfräser nach Anspruch 1 - 4, wobei das Sinterhartmetall-Substrat eine Zusammensetzung aus 5 - 20 Gew.-% Co als Binderphase bildende Komponente, 0,1 - 2 Gew.-% Cr und/oder V als Binderphase bildende Komponente, 0,1 - 5 Gew.-% von einer oder mehr Arten von Carbiden oder Nitriden von Ti, Ta, Nb und Zr genauso wie zwei oder mehr Arten von festen Lösungen davon als dispergierte Phase bildende Komponente aufweist, und der Rest Wolframcarbid als dispergierte Phase bildende Komponente und unvermeid-

bare Verunreinigungen ist.

### Revendications

5. 1. Fraise à queue en carbure cémenté revêtue pourvue de couches en matériaux durs ayant une excellente adhésion, comprenant un substrat en carbure cémenté à base de carbure de tungstène, dans laquelle le carbure de tungstène a une structure de particule fine ayant une taille de particule moyenne de 0,1-1,5 µm, le substrat en carbure de tungstène a une couche de surface dans laquelle du carbure ( $\text{CO}_m\text{W}_n\text{C}$ ) est réparti sur une profondeur de 0,1-2 µm de la surface la plus extérieure au niveau du bord tranchant de celle-ci et le substrat en carbure cémenté est encore pourvu de couches en matériaux durs composées d'une couche en composé de Ti formée sur celle-ci dans une épaisseur de couche moyenne de 0,5-4,5 µm, la couche en composé de Ti étant constituée d'une ou de plusieurs couches de TiC, TiN, TiCN, TiCO, TiNO et TiCNO.
15. 2. Fraise à queue en carbure cémenté revêtue pourvue de couches en matériaux durs ayant une excellente adhésion, comprenant un substrat en carbure cémenté à base de carbure de tungstène, dans laquelle le carbure de tungstène a une structure de particule fine ayant une taille de particule moyenne de 0,1-1,5 µm, le substrat en carbure de tungstène a une couche de surface dans laquelle du carbure ( $\text{CO}_m\text{W}_n\text{C}$ ) est réparti sur une profondeur de 0,1-2 µm de la surface la plus extérieure au niveau du bord tranchant de celle-ci et le substrat en carbure cémenté est encore pourvu de couches en matériaux durs composées d'une couche en composé de Ti et d'une couche en  $\text{Al}_2\text{O}_3$  formées sur celle-ci dans une épaisseur de couche moyenne de 0,5-4,5 µm, la couche en composé de Ti étant constituée d'une ou de plusieurs couches de TiC, TiN, TiCN, TiCO, TiNO, TiCNO.
25. 3. Fraise à queue en carbure cémenté revêtue pourvue de couches en matériaux durs ayant une excellente adhésion, comprenant un substrat en carbure cémenté à base de carbure de tungstène, dans laquelle le carbure de tungstène a une structure de particule fine ayant une taille de particule moyenne de 0,1-1,5 µm, le substrat en carbure de tungstène a une couche de surface formée sur la portion de surface de celle-ci qui est formée par chauffage à haute température et dans laquelle du carbure ( $\text{CO}_m\text{W}_n\text{C}$ ) créé par la réaction de Co et de W est réparti sur une profondeur de 0,1-2 µm de la surface la plus extérieure au niveau du bord tranchant de celle-ci et le substrat en carbure cémenté est encore pourvu de couches en matériaux durs composées d'une couche en composé de Ti formée sur celle-ci dans une épaisseur de couche moyenne de 0,5-4,5 µm, la couche en composé de Ti étant constituée d'une ou de plusieurs couches de TiC, TiN, TiCN, TiCO, TiNO, TiCNO formées par dépôt chimique en phase vapeur à température moyenne à une température de 700-980 °C.
35. 4. Fraise à queue en carbure cémenté revêtue pourvue de couches en matériaux durs ayant une excellente adhésion, comprenant un substrat en carbure cémenté à base de carbure de tungstène, dans laquelle le carbure de tungstène a une structure de particule fine ayant une taille de particule moyenne de 0,1-1,5 µm, le substrat en carbure de tungstène a une couche de surface formée sur la portion de surface de celle-ci qui est formée par chauffage à haute température et dans laquelle du carbure ( $\text{CO}_m\text{W}_n\text{C}$ ) créé par réaction de Co et de W est réparti sur une profondeur de 0,1-2 µm de la surface la plus extérieure au niveau du bord tranchant de celle-ci et le substrat en carbure cémenté est encore pourvu de couches en matériaux durs composées d'une couche en composé de Ti et d'une couche en  $\text{Al}_2\text{O}_3$  formées sur celle-ci dans une épaisseur de couche moyenne de 0,5-4,5 µm, la couche en composé de Ti étant constituée d'une ou de plusieurs couches de TiC, TiN, TiCN, TiCO, TiNO, TiCNO formées par dépôt chimique en phase vapeur à température moyenne à une température de 700-980 °C.
45. 5. Fraise à queue en carbure cémenté revêtue selon les revendications 1 à 4, dans laquelle ledit substrat en carbure cémenté a une composition de 5-20 % en poids de Co en tant que composant formant une phase de liant, le reste étant du carbure de tungstène sous la forme d'un composant formant une phase dispersée et des impuretés inévitables.
50. 6. Fraise à queue en carbure cémenté revêtue selon les revendications 1 à 4, dans laquelle ledit substrat en carbure cémenté a une composition de 5-20 % en poids de Co en tant que composant formant une phase de liant, 0,1-2 % en poids de Cr et/ou de V en tant que composant formant une phase de liant, le reste étant du carbure de tungstène sous la forme d'un composant formant une phase dispersée et des impuretés inévitables.
55. 7. Fraise à queue en carbure cémenté revêtue selon les revendications 1 à 4, dans laquelle ledit substrat en carbure cémenté a une composition de 5-20 % en poids de Co en tant que composant formant une phase de liant, 0,1-5 % en poids d'un ou de plusieurs types de carbures et de nitrures de Ti, Ta, Nb et Zr, ainsi que deux types ou plus

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de solutions solides de ceux-ci sous la forme d'un composant formant une phase dispersée, le reste étant du carbure de tungstène sous la forme d'un composant formant une phase dispersée et des impuretés inévitables.

- 5       8. Fraise à queue en carbure cémenté revêtue selon les revendications 1 à 4, dans laquelle ledit substrat en carbure cémenté a une composition de 5-20 % en poids de Co en tant que composant formant une phase de liant, 0,1-2 % en poids de Cr et/ou de V en tant que composant formant une phase de liant, 0,1-5 % en poids d'un ou de plusieurs types de carbures et de nitrures de Ti, Ta, Nb et Zr, ainsi que deux types ou plus de solutions solides de ceux-ci sous la forme d'un composant formant une phase dispersée, le reste étant du carbure de tungstène sous la forme d'un composant formant une phase dispersée et des impuretés inévitables.

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